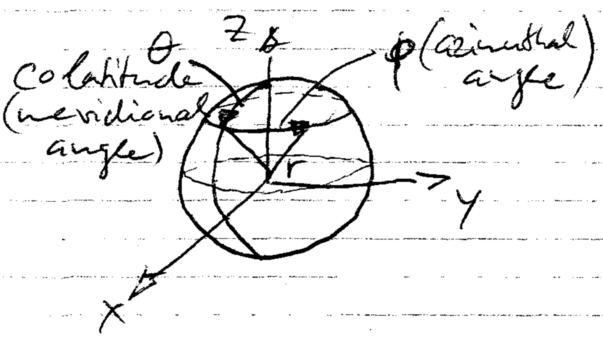
ROTATION IN 3D: PARTICLE ON SPHERE

Spherical polar coordinates: r, θ, ϕ



$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \text{(Laplacian)}$$

del-squared

nabla-squared

$\theta = [0, \pi]$

$\phi = [0, 2\pi]$

particle confined to surface: $r = \text{const}$

$\Rightarrow \psi = \psi(\theta, \phi)$ $\qquad V = 0$

separation of variables: $\psi(\theta,\phi) = \Theta(\theta)\cdot\Phi(\phi)$

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2 \quad \text{(spherical polar coordinates)}$$

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} \quad \text{(Legendrian)}$$

$r = \text{const.}$

$$\Rightarrow \text{SE:} \quad \frac{1}{r^2}\Lambda^2\psi = -\frac{2mE}{\hbar}\psi$$

$I = mr^2$

$\varepsilon = \frac{2IE}{\hbar^2}$

$$\Lambda^2\psi = -\varepsilon\psi$$

insert $\psi(\theta,\phi) = \Theta(\theta)\Phi(\phi)$

$$\frac{1}{\sin^2\theta}\frac{\partial^2(\Theta\Phi)}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial(\Theta\Phi)}{\partial\theta} = -\varepsilon\Theta\Phi$$

$$\frac{\Theta}{\sin^2\theta}\frac{d^2\Phi}{d\phi^2} + \frac{\Phi}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} = -\varepsilon\Theta\Phi$$

$$\underbrace{\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}}_{\substack{=\text{const.}\\ \text{say } -m_l^2}} + \underbrace{\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + \varepsilon\sin^2\theta}_{\substack{=\text{const.}\\ \text{say: } m_l^2}} = 0$$

- $\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = -m_l^2$

  same as before for 2D (particle on ring)

  $\Phi_{m_l}(\varphi) = \frac{e^{im_l\varphi}}{\sqrt{2\pi}}$, $m_l = 0, \pm 1, \ldots$

- $\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + \varepsilon\sin^2\theta = m_l^2$

  Solutions are "associated Legendre functions"

  ~~the boundary conditions~~

  $P_l^{m_l}(\cos\theta)$, $\omega = \cos\theta$

  Legendre Polynomials:

  $P_l(\omega) = \frac{1}{2^l l!}\frac{d^l}{d\omega^l}(\omega^2-1)^l$ — solve DE for $m_l = 0$

  $P_0(\omega) = 1$

  $P_1(\omega) = \omega$

  $P_2(\omega) = \frac{1}{2}(3\omega^2 - 1)$

  $P_3(\omega) = \frac{1}{2}(5\omega^3 - 3\omega)$

  $\vdots$

  recursion relation:

  $(2l+1)\omega P_l - (l+1)P_{l+1} - lP_{l-1} = 0$

  $\Rightarrow$ associated Legendre functions $P_l^{m_l}(\omega)$ (also $m_l \neq 0$)

  $P_l^{m_l}(\omega) = (1-\omega^2)^{m_l/2}\frac{d^{m_l}}{d\omega^{m_l}}P_l(\omega)$, $m = 0, 1, 2, \ldots l$

  recurrence relation:

  $(2l+1)\omega P_l^{m_l} = (l+1-m_l)P_{l+1}^{m_l} + (l+m_l)P_{l-1}^{m_l}$

  $P_1^1(\omega) = (1-\omega^2)^{1/2}$

  $P_2^1(\omega) = 3(1-\omega^2)^{1/2}\omega$

  $P_3^1(\omega) = \frac{3}{2}(1-\omega^2)^{1/2}(5\omega^2-1)$

  $P_2^2(\omega) = \cancel{15\omega(1-\omega^2)}\; 3(1-\omega^2)$

  $P_3^2(\omega) = 15\omega(1-\omega^2)$

  $P_3^3(\omega) = 15(1-\omega^2)^{3/2}$

  $\vdots$

move back to ($\ast$)

- cyclic boundary conditions for θ lead to additional quantization
  $\Rightarrow$ quantum number $\ell = 0, 1, 2, \ldots$
  orbital angular momentum quantum number
- ($\ast$) since m_ℓ appears in DE for θ there is an additional restriction on this quantum number

$$m_\ell = \ell, (\ell-1), (\ell-2), \ldots, -(\ell-1), -\ell$$

magnetic quantum number

$\Rightarrow$ for each ℓ there are $2\ell+1$ permitted m_ℓ

$$\Theta_{\ell m_\ell}(\theta) = \begin{cases} (-1)^m \left[\dfrac{(2\ell+1)(\ell-m_\ell)!}{2(\ell+m)!}\right]^{1/2} P_\ell^{m_\ell}(\cos\theta) & m_\ell \geq 0 \\ (-1)^{|m|}\, \Theta_{\ell|m|}(\theta) & m < 0 \end{cases}$$

Finally: (drop subscript $m_\ell = m$)

$$\psi(\theta,\varphi) = \Theta_{\ell m}(\theta)\, \Phi_m(\varphi) = Y_{\ell m}(\theta,\varphi)$$

"spherical harmonics"

$$\boxed{\begin{aligned} Y_{\ell m}(\theta,\varphi) &= (-1)^m \left[\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}\right]^{1/2} P_\ell^m(\cos\theta)\, e^{im\varphi}, \quad m \geq 0 \\ Y_{\ell,-m}(\theta,\varphi) &= (-1)^m\, Y^*_{\ell m}(\theta,\varphi) \end{aligned}}$$

(they are orthonormal)

ℓ	m	$Y_{\ell m}$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
1	± 1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\varphi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos\theta - 1)$
$\vdots$		

(for ~~complete~~ longer list see ~~[illegible]~~ Atkins, Table 12.3 or Bransden, Table 2.1

- The $Y_{lm}(\theta,\varphi)$ are eigenfunctions of the $\hat{L}^2$ operator (orbital momentum squared)

$$\hat{L}^2 = -\hbar^2 \Lambda^2$$

$$\hat{L}^2 Y_{lm}(\theta,\varphi) = l(l+1)\hbar^2 Y_{lm}(\theta,\varphi)$$

For rotation of particle on sphere (rigid rotator)

$$\hat{H} = \frac{\hat{L}^2}{2I} \left(= -\frac{\hbar^2}{2I}\Lambda^2 \right)$$

$$\Rightarrow \hat{H} Y_{lm}(\theta,\varphi) = E\, Y_{lm}(\theta,\varphi) = \frac{l(l+1)\hbar^2}{2I}$$

$$\Rightarrow \boxed{E_L = \frac{\hbar^2}{2I}\, l(l+1) \qquad l = 0, 1, 2, \ldots}$$

(*)

- energy is quantized and independent of m
- there are $2l+1$ different wave functions for each l (each w/ different m)

  $\Rightarrow$ Energy levels are $(2l+1)$-fold degenerate (only amount of orbital momentum, not its direction important for energy)

- The $Y_{lm}(\theta,\varphi)$ are also eigenfunctions of the

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$ operator (z-component of orbital momentum)

$$\hat{L}_z Y_{lm}(\theta,\varphi) = m\hbar\, \Psi_{ml} \quad ; m = -l, -(l+1), \ldots l$$

$\Rightarrow$ also z-component of angular momentum is quantized (no influence on energy though)

Orbital momentum is quantized

$$L^2 = l(l+1)\hbar^2 \quad , \; l = 0, 1, 2, \ldots$$

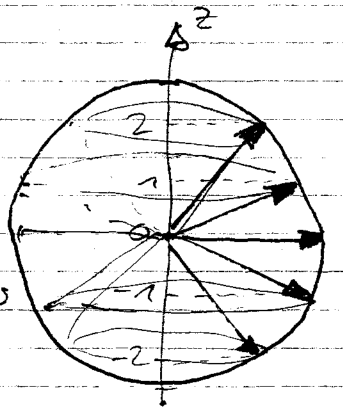
z-component of momentum is also quantized

$$L_z = m\hbar \quad , \; m = 0, \pm 1, \ldots, \pm l$$

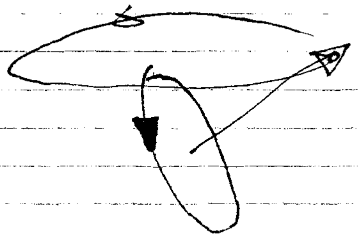
$l = 2$

$\Rightarrow |L| = \sqrt{5}\,\hbar$

$2l+1 = 5$ m values



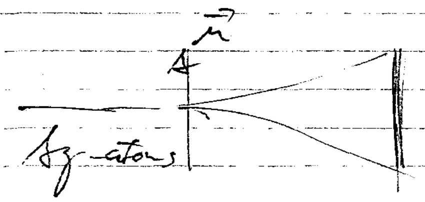
$\Rightarrow$ the orientation of a rotating body is quantized!



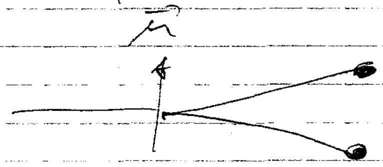
only projection onto z-axis is known, projections on x- or y-axis are indefinite, why? $[L_x, L_z] \neq 0$; $[L_z, L_y] \neq$ They do not commute

but no azimuthal quantization!

confirmed by Stern-Gerlach experiment



classically $\Rightarrow$



QM ✓

But: $2l+1 = 2 \Leftrightarrow l = \frac{1}{2}$??

$\Rightarrow$ not orbital angular momentum of ~~[illegible]~~ electron around atom (rotation on a sphere as Bohr-like model)

but: rotation of e^- around its own axis

This intrinsic motion of electrons is called <u>spin</u>

(explanation comes from combination of QM and special relativity $\rightarrow$ relativistic quantum mechanics)

$$S^2 = s(s+1)\hbar^2 \quad , \; s > 0 \; \text{(spin quantum number)}$$

$$S_z = m_s \hbar \quad , \; m_s = 0, \pm\tfrac{1}{2}, 1, \ldots, \pm s$$

(spin magnetic quantum number)

For electron: $s = \frac{1}{2}$ is the only possible value

$\Rightarrow 2s+1 = 2$ possible orientations

$m_s = \pm \frac{1}{2}$ $\left(\begin{matrix} + & \alpha & \uparrow \\ - & \beta & \downarrow \end{matrix}\right)$

($\Rightarrow$ Stern-Gerlach: $Ag = [Kr]\, 4d^{10}\, 5s^1$

$\Rightarrow$ one unpaired electron determines angular moment

- $s = \frac{1}{2}$: electron, proton, neutrons (fermions) half integer spin
  $s = 1$: photon, mesons, (boson; integer spin)

fermions: elementary particles $\Rightarrow$ ~~matter~~ } matter
bosons: mediate forces between fermions }

Notation: l, m_l $\Rightarrow$ orbital angular moment (orientation in space)

s, m_s $\Rightarrow$ spin (intrinsic angular moment)

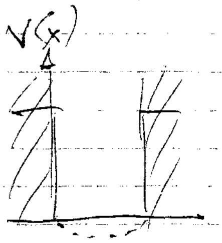
j, m_j $\Rightarrow$ combination of both

TECHNIQUES OF APPROXIMATION

- so far: simple scenarios w/ exact solutions
- in general (especially w/ larger atoms + molecules) no exact solutions can be found
- approximation by (variation theory) and perturbation th. later

TIME-INDEPENDENT PERTURBATION THEORY

Perturbation theory: $H^{(0)}$ has known eigenfunctions + values



$H^{(1)}$ represents difference btw 'model' and true hamiltonian

$$H = H^{(0)} + \lambda H^{(1)}$$

(λ is a variable that helps to keep track of orders but is set to unity at the end)

$-E\sin\left(\frac{\pi x}{L}\right)$

here: $H^{(1)} \neq H^{(1)}(t)$ does not vary over time $\Rightarrow$ constant perturbation

$$\Rightarrow E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots$$

$E^{(1)}$ first-order,

$E^{(2)}$ second-order correction to the energy

~~A~~lso: $\psi = \psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \dots$

We usually only consider first-order corrections.

Insert H and ψ into Schrödinger Equation:

$$(H^{(0)} + \lambda H^{(1)})(\psi^{(0)} + \lambda\cdot\psi^{(1)} + \lambda^2\psi^{(2)} + \dots) =$$
$$(E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots)(\psi^{(0)} + \lambda\psi^{(1)} + \psi^2\psi^{(2)})$$

$$H^{(0)}\psi^{(0)} + \lambda(H^{(1)}\psi^{(0)} + H^{(0)}\psi^{(1)}) + \lambda^2(H^{(0)}\psi^{(2)} + H^{(1)}\psi^{(1)} + \dots) =$$
$$= E^{(0)}\psi^{(0)} + \lambda(E^{(0)}\psi^{(1)} + E^{(1)}\psi^{(0)}) + \lambda^2(E^{(2)}\psi^{(0)} + E^{(1)}\psi^{(1)} + E^{(0)}\psi^{(2)} + \dots)$$

True for any state n, here now for $n=0$:

λ^0: $H^{(0)}\psi_0^{(0)} = E_0^{(0)}\psi_0^{(0)}$ (S.E. for ground/unperturbed state); known $\psi_0, E_0, H_0 \in$ ground state

λ^1: $H^{(1)}\psi_0^{(0)} + H^{(0)}\psi_0^{(1)} = E_0^{(0)}\psi_0^{(1)} + E_0^{(1)}\psi_0^{(0)}$

Suppose: $\psi_0^{(1)} = \sum_n c_n \psi_n^{(0)}$

first-order correction is linear combination of wavefunctions of unperturbed system